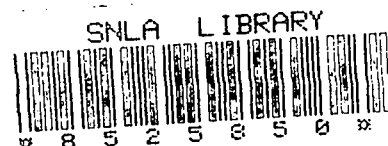


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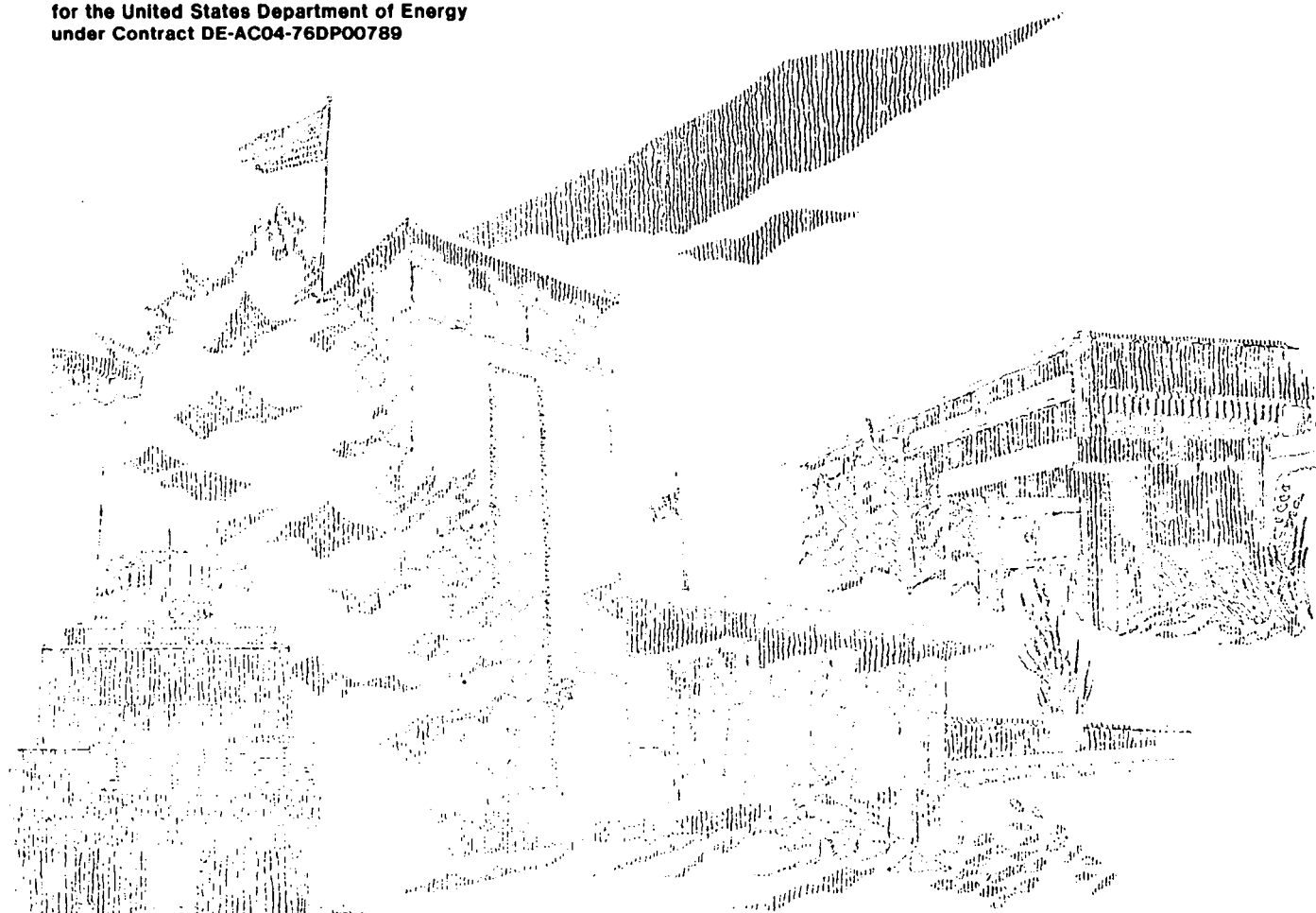
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MICROFICHE**Durability of Carbon-Plastic Electrodes
for Zinc/Bromine Storage Batteries**

Charles Arnold, Jr.

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
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Durability of Carbon-Plastic Electrodes for Zinc/Bromine Storage Batteries

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Abstract

In previous work, failure of early versions of the zinc/bromine battery was traced to degradation and warpage of the carbon-plastic electrode. These electrodes were fabricated from copolymers of ethylene and propylene (EP) containing structures that were found to be susceptible to degradation by the electrolyte. In this work, we evaluated two developmental electrodes from Johnson Controls Battery Group, Inc., in which the EP copolymer was replaced with a high-density polyethylene (HDPE) that contained glass-fiber reinforcing fillers. The glass fiber content of these two electrodes was different (19% vs. 31%). In this work, we evaluated the effect of Johnson Controls' electrolyte on these electrodes. Specifically, we determined the effect of the electrolyte on sorption behavior, dimensional stability, chemical stability, and thermal, mechanical, and electrical properties under real-time and accelerated aging conditions. We also characterized *unaged* samples of both electrodes to determine their chemical composition and physical structure. We found that high glass content in the electrode minimizes sorption and increases dimensional stability. Both high and low glass content electrodes were found to be chemically and thermally stable toward the electrolyte. A slight decrease in the storage modulus (G') of both electrodes was attributed to sorption of non-ionic and hydrophobic ingredients in the electrolyte. The electrical conductivity of both electrodes appeared to improve (increase) upon exposure to the electrolyte. No time or temperature trends were observed for the chemical, thermal, or mechanical properties of electrodes made from HDPE. Since decreases in these properties were noted for electrodes made from EP copolymers under similar conditions, it appears that the HDPE-based electrodes have superior long-term stability in the ZnBr_2 environment.

Acknowledgments

The author thanks J. S. Miller, 1811, for her technical assistance, and Gary Zender, 1822, for providing the SEM and EDAX data on the unaged samples.

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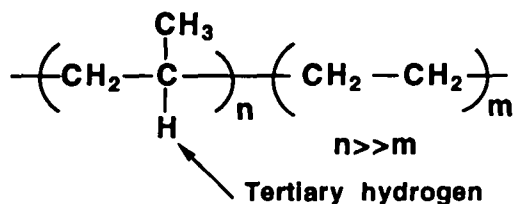
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Durability of Carbon-Plastic Electrodes for Zinc/Bromine Storage Batteries

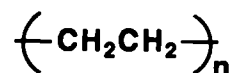
Introduction

The lifetimes of zinc/bromine batteries may be limited by the durability of the thermoplastic components that are exposed to the bromine-containing electrolytes used in these batteries. One example of such a component is the bipolar carbon-plastic electrode. In early versions of the zinc/bromine battery, these electrodes were fabricated from copolymers of ethylene and propylene (EP copolymers). In previous durability studies, it was found that carbon-plastic electrodes made from propylene-rich EP copolymers warped during the operation of the battery, resulting ultimately in failure of the battery. Postmortem analyses revealed that the plastic component, namely the propylene-rich EP copolymer, had been oxidatively attacked by the electrolyte.¹ This chemical attack was believed to have exacerbated the warpage problem by enhancing the hydrophilicity of the electrode which, in turn, caused a higher degree of swelling. The susceptibility of EP copolymers to oxidative attack was attributed to the presence of a large number of tertiary hydrogens in the backbone of these polymers. The tertiary hydrogens occur at the branch points in the propylene units in the chain as shown below.



EP Copolymer

It is well known that such structures are vulnerable to thermoxidative degradation.² Improvements in oxidative stability should be made possible by eliminating most, if not all, of the tertiary hydrogens. This can be achieved by replacing the EP copolymer with an unbranched version of polyethylene, i.e., high-density polyethylene (HDPE). The simple structure of HDPE is shown as follows.



Personnel at Johnson Controls Corp. formulated two HDPE-based carbon-plastic electrodes having different glass-fiber contents. We designated these electrodes HDPE-1 and HDPE-2.

The purpose of this study was to evaluate the stability of these electrodes toward an electrolyte used by Johnson Controls in its zinc/bromine battery. To accomplish this, we monitored the following properties under real-time and accelerated aging conditions: mass, dimensions (length, width, and thickness), shear modulus (G'), G' versus temperature, melting temperature, heat of fusion, and electrical conductivity. In addition, FTIR analyses were carried out on aged and unaged samples of the electrodes to detect chemical structural changes attributed to degradation by the electrolyte.

Experimental

Materials. The synthetic electrolyte in which the aging experiments were carried out had the following composition: 1.0 M zinc bromide; 3.5 M ammonium chloride; 0.8 M methyl ethyl morpholinium (MEM) bromide; 0.8 M methyl ethyl pyrrolidinium (MEP) bromide; and 2.0 M bromine. MEM and MEP are bromine complexing agents obtained by courtesy of the Exxon Co. All of these electrolyte ingredients were used as received.

Aging Conditions. The aging conditions used in this study are shown in Table 1. In the ambient temperature runs, all of the samples were placed in two 2-liter flasks, each containing 1 liter of the two-phase electrolyte and agitated using an Orbital Lab shaker table. The dimensions of the samples were 2.3 in. \times 0.5 in. \times 0.048 in. for HDPE-1 and 2.3 in. \times 0.5 in. \times 0.023 in. for HDPE-2. The samples were removed for analysis after 1, 3, and 6 months' exposure. In the accelerated aging experiments, the electrodes were aged at 40°C, 50°C, and 60°C in the

upper aqueous phase of the two-phase electrolyte contained in 75-mL screwcap vials. To ensure there was no loss of electrolyte, the caps were lined with Parawax film. In these runs, the electrodes were in contact with the relatively small concentration of free bromine that is in equilibrium with the complexed bromine in the lower phase. Under comparable conditions, degradation of electrodes made from EP copolymers had been observed in previous studies.¹

Electrode Characterization. The methods used to characterize both the unaged and aged electrodes are summarized in Table 2. This table also provides information on the types of properties evaluated and our reasons for choosing a particular property. Unaged electrodes were characterized for two reasons: (1) to determine the composition and morphology of the electrodes; and (2) to determine baseline properties so as to detect degradation. Other information included in this table is self-explanatory.

Table 1. Aging Matrix

TEMPERATURE (C)			TIME (Months)	
		1	3	6
Ambient		X	X	X
40		X	X	X
50		X	X	X
60		X	X	X

Table 2. Characterization of Aged and Unaged Electrodes

Property Class	Property	Method(s)	Purpose of Test	Instrument ID	Comments
Macro-Structure	ID and distribution of component materials	Scanning electron microscopy (SEM)/EDAX	Determine uniformity and identity of fillers for unaged samples	Jeol 6400 with a Tracor-Northern EDS (X-ray) accessory	
Composition	Weight loss vs temperature	Thermogravimetric analysis (TGA)	Determine glass filler content for unaged samples	Perkin Elmer 7500 System 7 TGA	Heating rate of 20C/min in air; temperature range was from RT to 800C
Composition	Trace inorganic elements	Inductively coupled mass spec analysis	Identify leachable elements that might impair battery performance	Elan 500 Inductively Coupled Plasma Mass Spec (Sciex Corp.)	
Composition	Chemical structure	Fourier transform infrared analysis (FTIR)	Monitor possible degradation processes	Perkin Elmer Model 1750 FTIR	
Mass	Sorption	Weight gain or loss	An index of swelling behavior	Mettler AE 5 place balance	Weight gains determined by two methods: 1)after wiping off excess surface liquids and air drying; and 2) after washing to remove the sorbed salts and air drying.
Dimensions	Length, width, thickness	Calipers and micrometer	An index of swelling behavior		
Thermal	Melting temp. and heat of fusion	Differential scanning calorimetry (DSC)	Monitor effect of possible degradation processes on thermal properties	Perkin Elmer 7500 System 7 DSC	Heating rate of 10C/min in nitrogen over temperature range of RT to 200C
Mechanical (dynamic)	Shear modulus (G')	Mechanical spectroscopy	Monitor effect of possible degradation processes on dynamic mechanical properties	Rheometrics Model RMS-800 mechanical spectrometer (RDS-11)	Established that stresses were linear when strain levels set at < 0.2%. Sample size 2.3" X 0.5".
Thermomechanical	Shear modulus (G') vs temperature	Mechanical spectroscopy	Monitor effect of possible degradation processes on thermomechanical properties	Rheometrics Model RMS-800 mechanical spectrometer (RDS-11)	Established that stresses were linear when strain levels set at < 0.2%. Sample size 2.3" X 0.5".
Electrical	Conductivity	4 Point probe	Monitor effect of possible degradation processes on conductivity	Four point probe fitted with a Keithly 220 current source and an HP3478A multimeter	1 milliamp of current was applied to sample; voltage limit < 10V. Sample size 1" X 1". Measurements made after washing and vacuum drying.

Results and Discussion

Characterization of the Unaged Electrodes

Figures 1 and 2 show SEM photographs of HDPE-1 and HDPE-2, respectively. In each of these figures, the upper photographs are views of opposite surfaces of the electrodes and the bottom photograph is a view of the fracture surface across the thickness dimension of the electrode. It is apparent from these photographs that the fiber density on the surface of these electrodes was relatively low compared to that of the fracture surface. This accounts for the smooth texture at the surface of these electrodes. Most of the fibers appear to be oriented parallel to the surface of the electrodes. These orientation effects are probably related to the condition used to mold or extrude the electrodes.

In some of the earlier bipolar electrodes used in the zinc/bromine battery, a high-surface-area carbon coating was applied to one side of the electrode.³ When installed in the battery, this high-surface-area side of the electrode was in contact with catholyte and served to increase the kinetics of the bromine electrochemistry. There is no evidence from the SEM photographs that any such coating was applied to HDPE-1 or HDPE-2.

Figures 3 and 4 show the results of x-ray analyses (EDAX) to determine the elemental composition of the carbon-plastic and glass-fiber portions of the electrodes. As expected, carbon was the predominant element detected in the smooth parts of the electrode, and the glass fibers were composed predominantly of oxygen, silicon, aluminum, and calcium.

The elemental analyses of the ashes of HDPE-1 and HDPE-2 found by inductively coupled mass spectroscopy are summarized in Table 3. The concentrations of aluminum and calcium were much higher in HDPE-2. This suggests a higher glass-fiber content for HDPE-2. The differences in concentration of the other elements are considered to be relatively insignificant, with the possible exception of iron. The iron concentration, which was higher in HDPE-2, might be a problem because iron is known to catalyze the formation of hydrogen at the anode.⁴

Thermogravimetric analyses, shown in Figure 5, confirmed that HDPE-2 did in fact have a higher glass-fiber content than HDPE-1 (31% vs. 19%). In these analyses, all of the organic constituents of the

electrodes were removed by combustion, leaving only the glass fibers as a residue.

Electrode Aging

Sorption. Figure 6 is a column chart showing total weight gain as a function of time and temperature for HDPE-1 and HDPE-2. These data were obtained by measuring the increase in weight after removal of the excess electrolyte from the surface of electrode by wiping and air-drying for 24 hours. After 1 month of aging in the electrolyte, no differences in sorption between HDPE-1 and HDPE-2 were discernible. For both electrodes, weight gains were relatively high (6% to 7.5%) relative to weight gains observed after longer exposure times (3% to 5.5%). This decrease in sorption with time is not understood. One possible explanation is that equilibrium between the absorption and desorption processes had not been reached at the earlier time periods.

After 6 months of aging, differences in sorption between HDPE-1 and HDPE-2 became apparent (Figure 7). These differences in sorption were significantly larger after washing (4.5% for HDPE-1 vs. ~1.5% for HDPE-2). Washing with water removes all of the soluble electrolyte salts, such as ammonium chloride and zinc bromide. Since HDPE-2 has a higher glass-fiber content than HDPE-1, these results suggest that absorption of the non-ionic and/or hydrophobic components of the electrolyte occurs mainly in the carbon-plastic part of the electrode. These components were not identified.

Dimensional Changes. Column charts depicting dimensional changes incurred by HDPE-1 and -2 as a result of accelerated and real-time aging are shown in Figures 8 through 10. The column magnitudes represent the average increase or decrease in length, width, or thickness for three samples. Despite considerable scatter in these data, the following general observations can be made:

1. With a few exceptions (RT/1 month, 60°C/1 month for length and 50°C/1 month for width), the percentage changes in length and width were less for HDPE-2 than for HDPE-1. Relative thickness increases, however, were higher for HDPE-2 at 60°C. The greater dimensional stability of HDPE-2 in the longer dimensions (i.e., length and width) is probably attributable to the higher glass-filler content of this electrode.

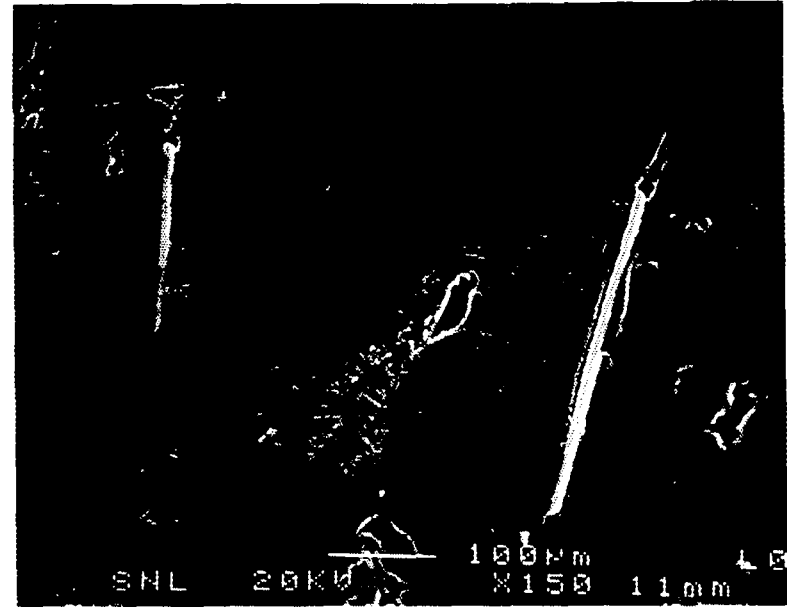


Figure 1. Scanning electron micrographs of HDPE-1. Upper photographs are opposite surfaces; lower photograph is the fracture surface.

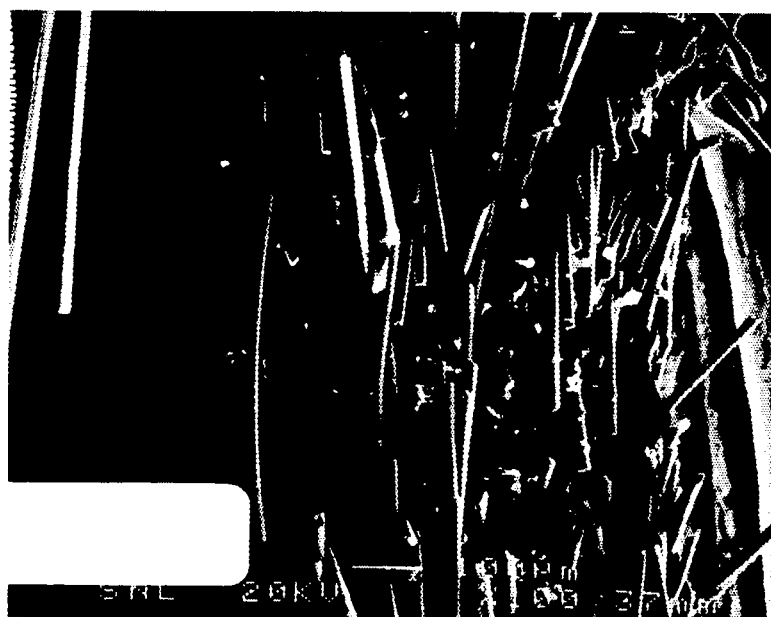
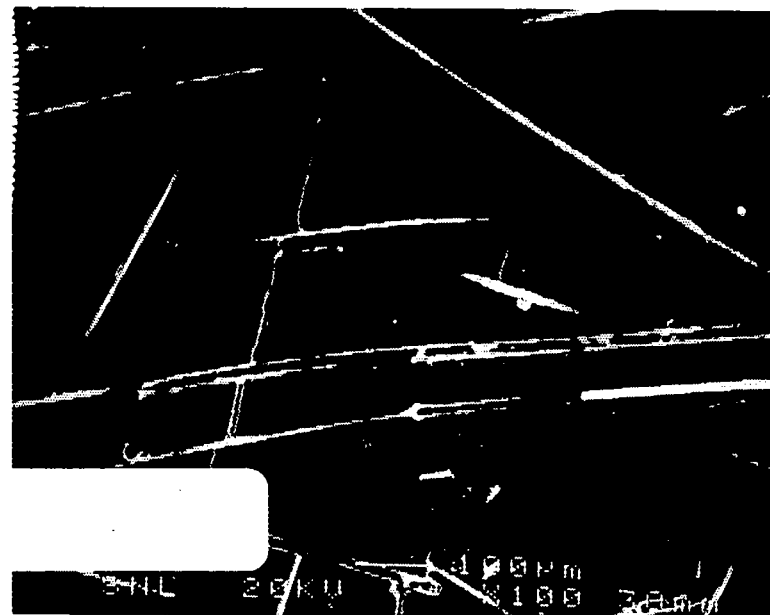
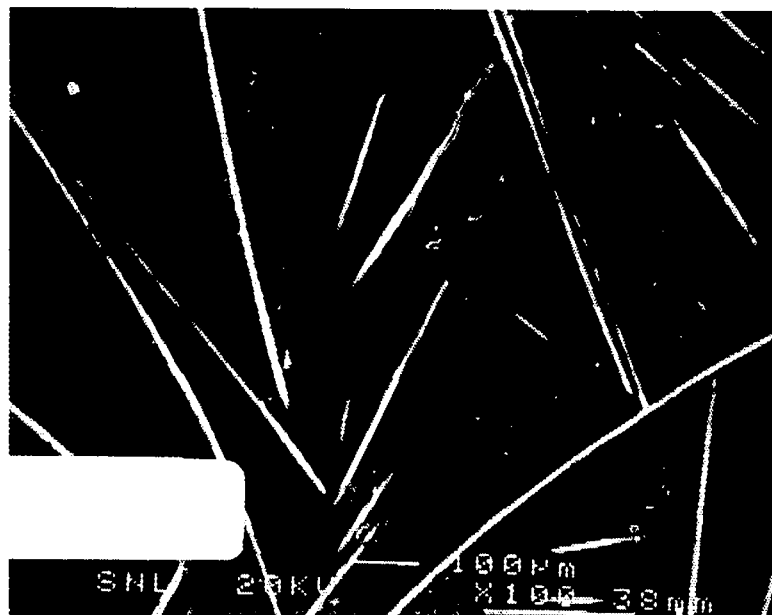


Figure 2. Scanning electron micrographs of HDPE-2. Upper photographs are opposite surfaces; lower photograph is the fracture surface.

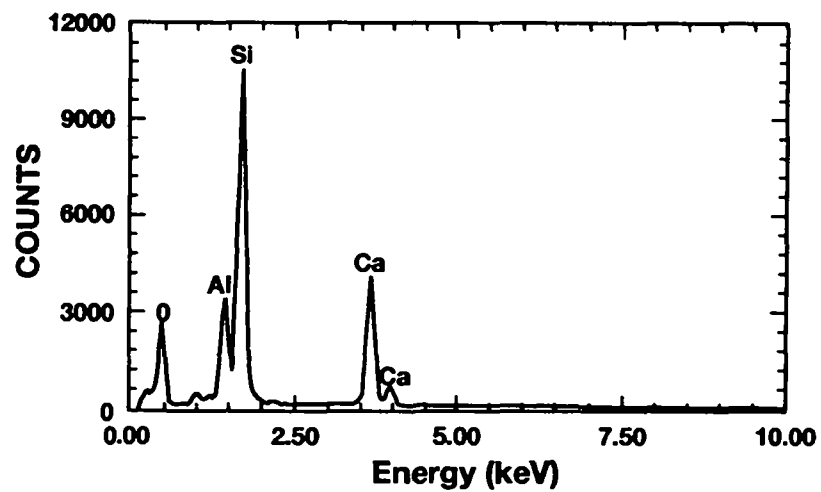
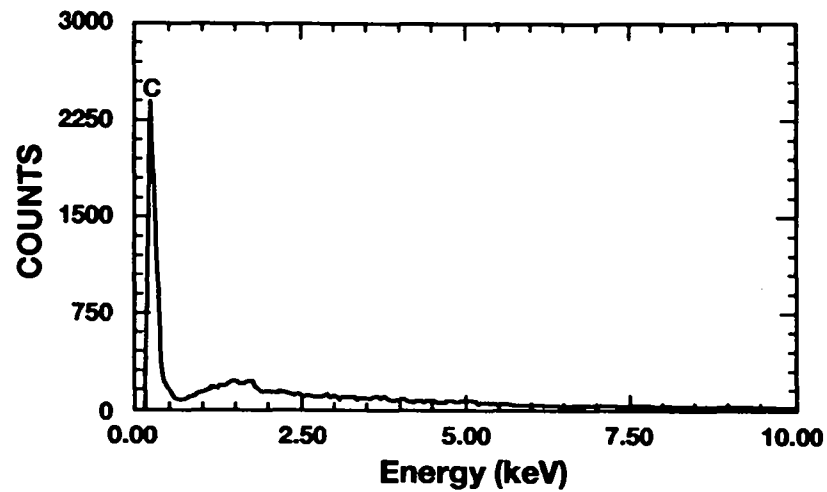
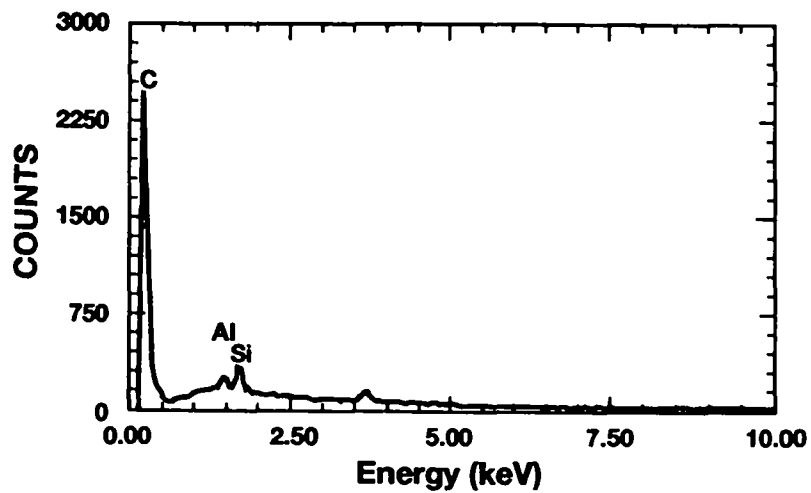


Figure 3. Elemental x-ray analyses of HDPE-1. Upper plots, carbon-plastic surfaces, show opposite sides; lower plot is the glass fiber on fracture surface.

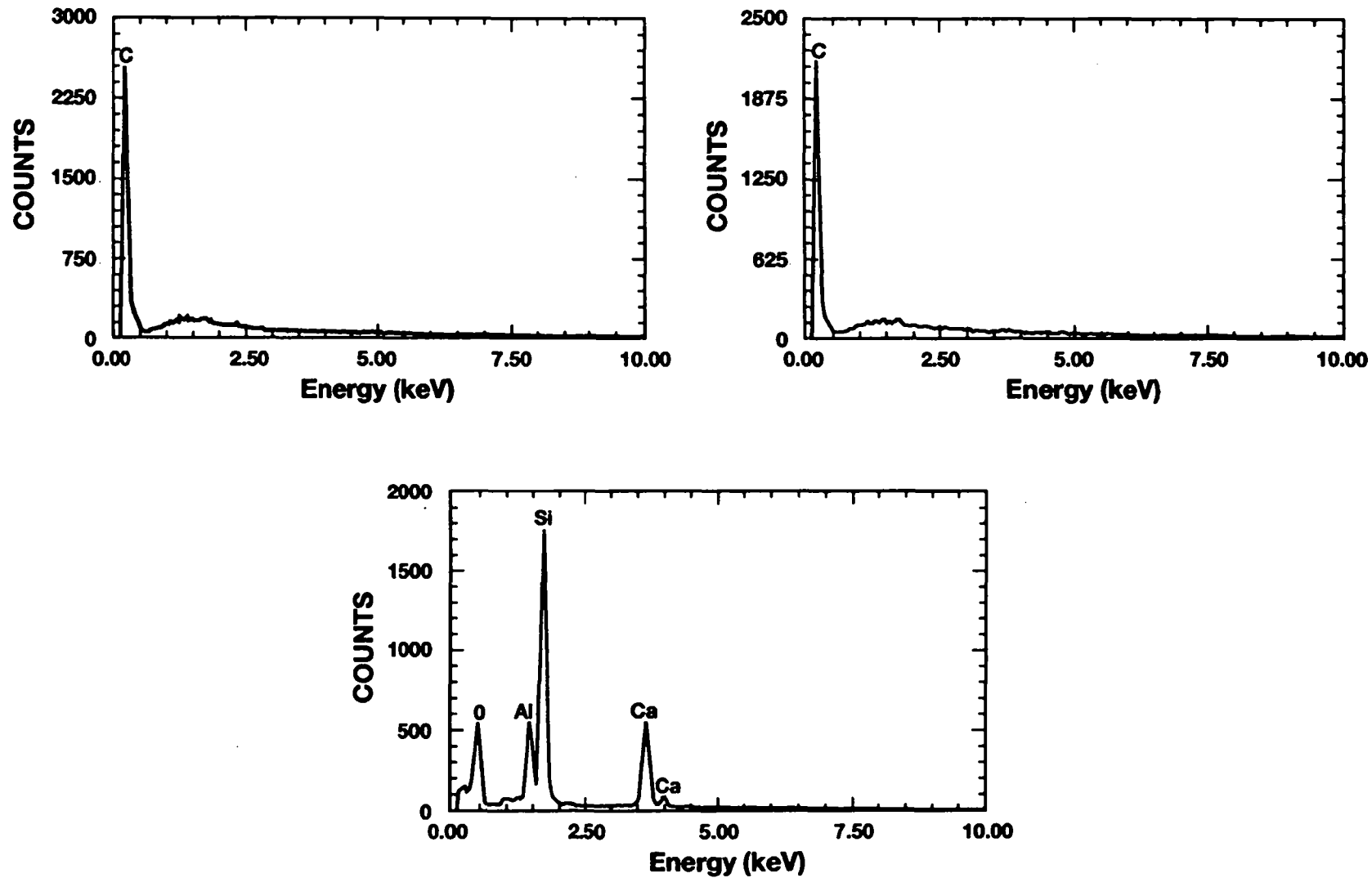


Figure 4. Elemental x-ray analyses of HDPE-2. Upper plots, carbon-plastic surfaces, show opposite sides; lower plot is the glass fiber on fracture surface.

Table 3. Inductively Coupled Mass Spectroscopic Analyses

Element	HDPE-1 (Conc. ppm)	HDPE-2 (conc. ppm)
Li	3	5
Na	7	13
Mg	4	20
Al	2960	13559
K	137	214
Ca	3080	15225
Ti	45	155
V	1	3
Cr	9	5
Mn	1	2
Fe	181	253
Co	0.9	0.4
Ni	9	2
Cu	1	2
Zn	3	23
Sn	19	27
Ba	1	3
Sr	16	84
Y	0.2	0.4
Zr	0.5	1
Pb	0.7	0.7

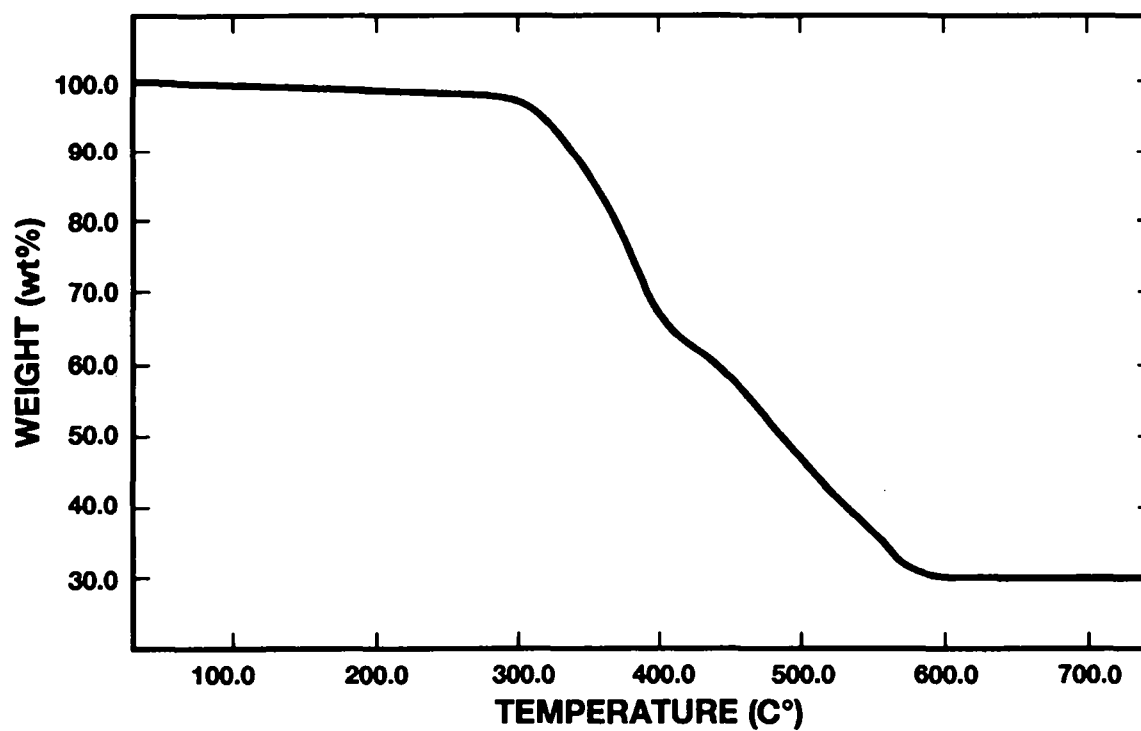
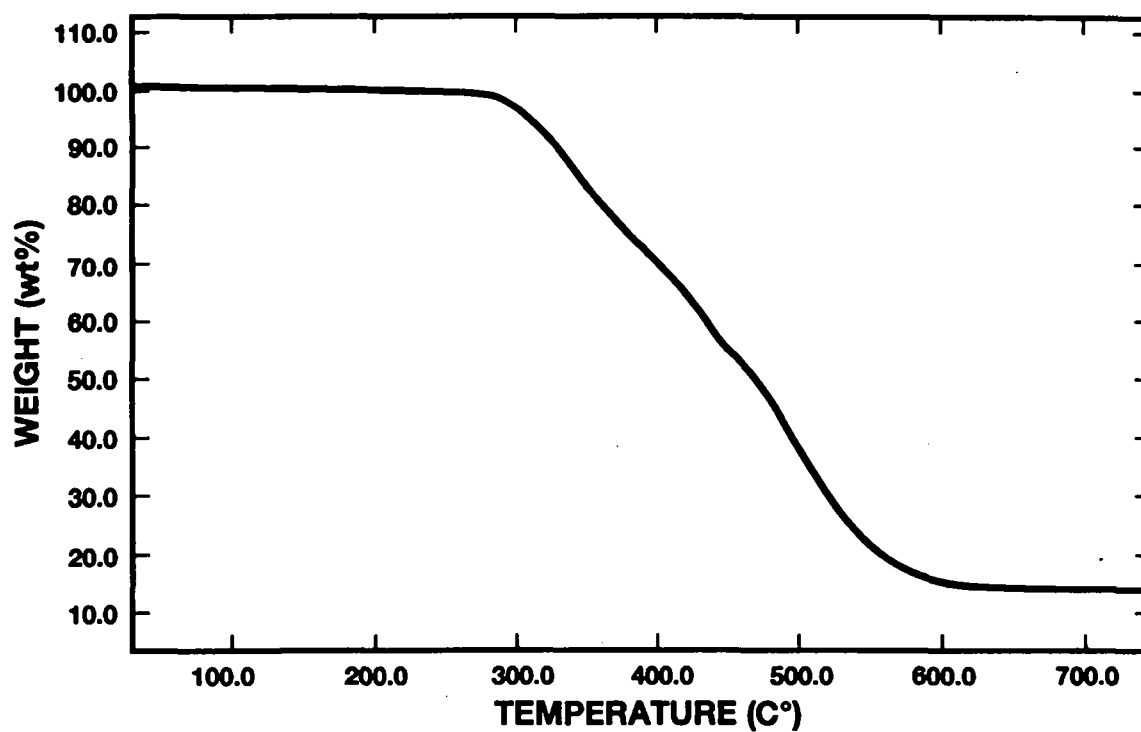


Figure 5. Thermogravimetric analyses performed in air at a heating rate of 20°C/min. Upper curve, HDPE-1; lower curve, HDPE-2.

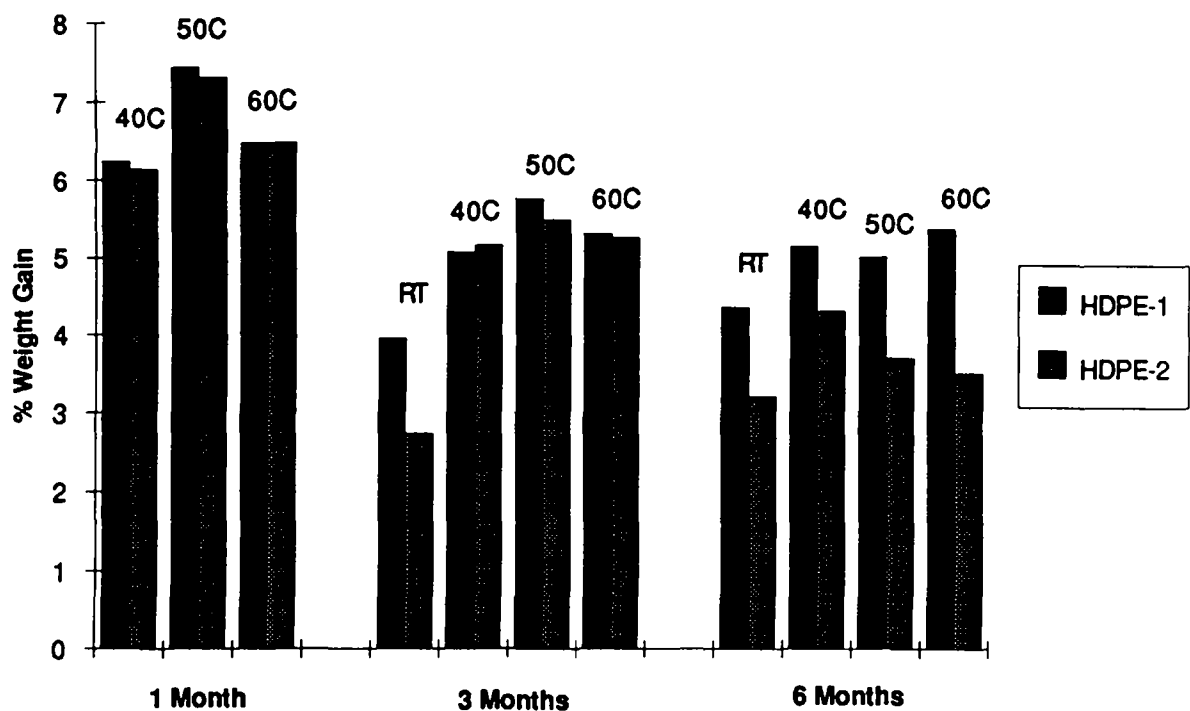


Figure 6. Column plot of percent sorption as a function of time and temperature for HDPE-1 and HDPE-2. Data represent weight gains after wiping off excess electrolyte and air-drying for 24 hours.

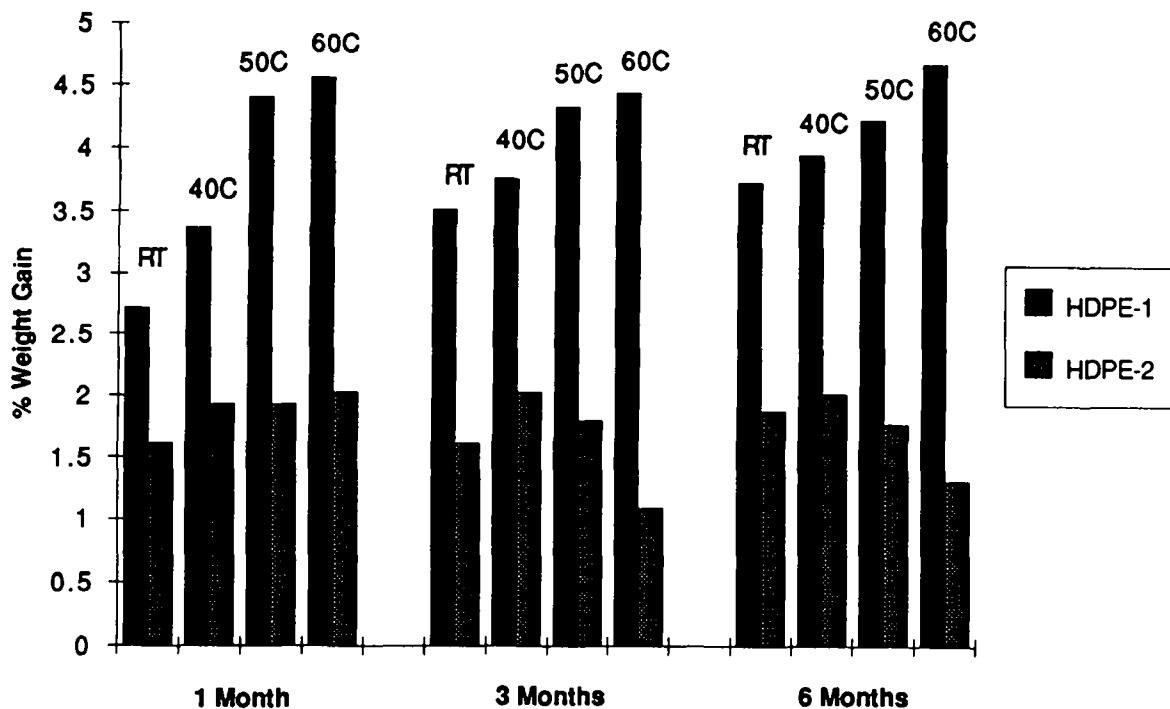


Figure 7. Column plot of percent sorption as a function of time and temperature for HDPE-1 and HDPE-2. Data represent weight gains after wiping off excess electrolyte and after washing to remove electrolyte salts and air-drying for 24 hours.

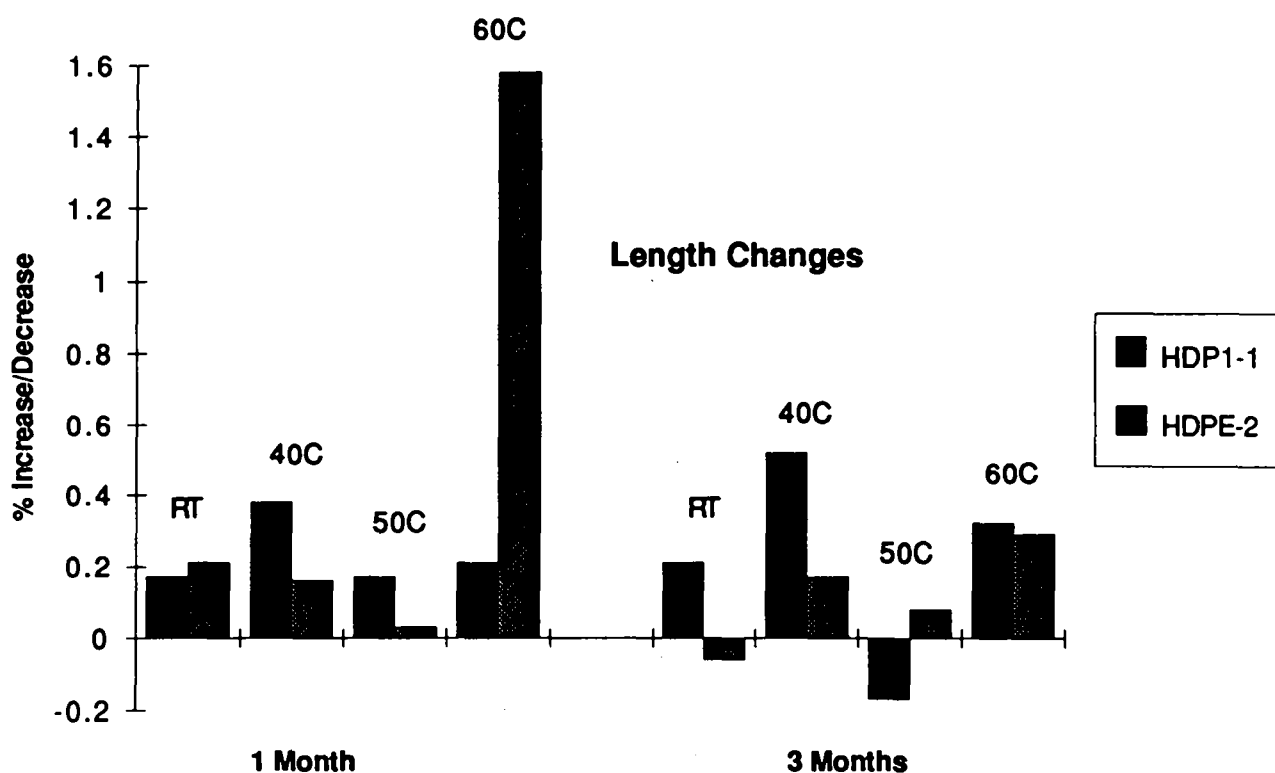


Figure 8. Column plot of percent changes in length as a function of time and temperature for HDPE-1 and HDPE-2. Dimensions were measured after a washing to remove excess electrolyte and after air-drying.

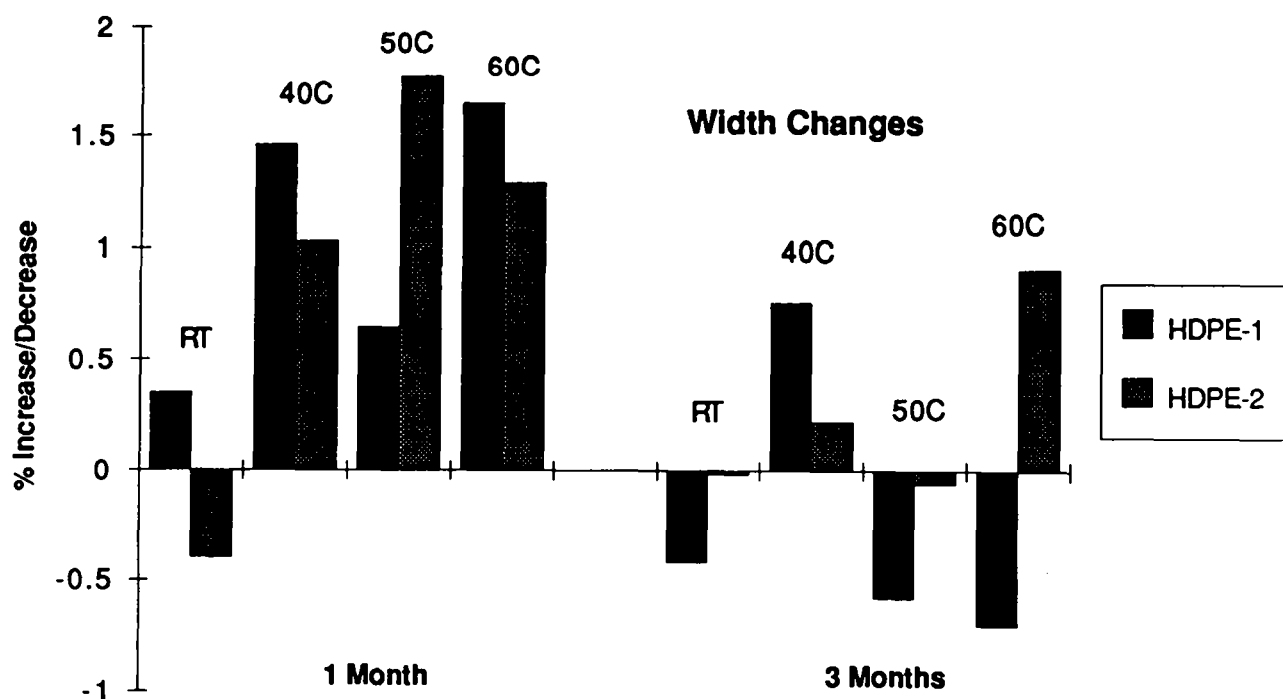


Figure 9. Column plot of percent changes in width as a function of time and temperature for HDPE-1 and HDPE-2. Dimensions were measured after a washing to remove excess electrolyte and after air-drying.

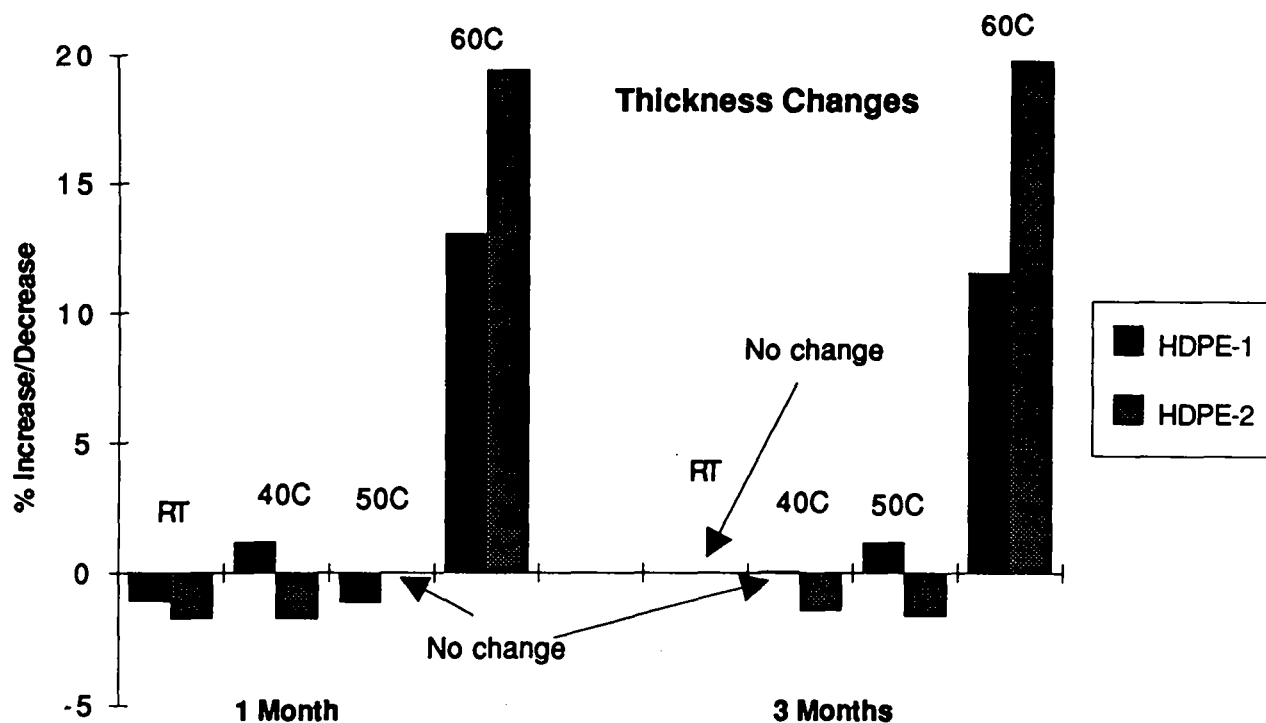


Figure 10. Column plot of percent changes in thickness as a function of time and temperature for HDPE-1 and HDPE-2. Dimensions were measured after a washing to remove excess electrolyte and after air-drying.

- On a percentage basis, the dimensional changes in thickness were greater than the dimensional changes in length and width for both electrodes. Thus, the following *ranges* of percentage changes for each dimension were: **thickness** (-1.5% to $+19\%$) $>$ **width** (-0.8% to $+1.7\%$) $>$ **length** (-0.13% to $+1.5\%$). The changes in length were skewed upward by one very high data point—namely, the 1-month 60°C point. If this data point is excluded, the range for length is reduced to 0.13% to 0.4% . On the basis of these data, one would expect that warpage would be less with HDPE-2, the electrode with the higher glass-fiber content. This expectation assumes that smaller percentage changes in the larger dimensions—namely, length and width—would have a greater detrimental effect on warpage than larger percentage changes in thickness.

Thermal Characterization. It is evident from the melting point and heat of fusion data shown in Table 4 that aging had little if any effect on the thermal properties of the electrodes. These properties are attributable to the polyethylene component of the electrode. While it is not known which brand of

polyethylene the battery developers used to make these electrodes, it is clear from the melting point that it was a linear, high-density type. Low-density polyethylenes have much lower melting points (100°C to 110°C). It is well known that the melting point of crystalline organic solids decrease when admixed with other compounds. The same is true for polymers. The melting of a polymer would be expected to decrease if degradation involving chain scission occurred. Since there was no difference in the melting point of unaged and aged specimens of the electrodes, it was concluded that either no degradation involving scission occurred or degradation was so small as to be undetectable by this method. The heat of fusion is a measure of the energy consumed during melting transition. As such, it is a measure of the degree of crystallinity present in the polymer. The fact that there were no trends for these data also suggests that the crystalline phase of the polymer was unaffected by exposure to the electrolyte. Degradation by processes other than chain scission can probably not be ruled out by melting point or heat of fusion type data. It is possible that some crosslinking of the polyethylene may have occurred. Crosslinking should lead to an increase in the storage modulus of the electrodes. As will be shown in the next section, this did *not* occur.

Table 4. Effect of Aging on Thermal Properties

Electrode	Temperature (C)	Time (months)	Melting Point (C)	Heat of Fusion (J/g)
HDPE-1	Control	0	125	-91.2
	Ambient	1	124.7	-88.1
	40	1	125.2	-88.5
	50	1	124.1	-85.4
	60	1	124	-86.1
	60	3	123.4	-88.4
	60	6	127.5	-89.2
HDPE-2	Control	0	124.8	-64.1
	Ambient	1	124.7	-70.8
	40	1	124.6	-67.2
	50	1	124.4	-72.8
	60	1	124.2	-68.7
	60	3	124.1	-67.8
	60	6	127.9	-72.2

Mechanical Characterization. The room temperature storage moduli (G') for HDPE-1 at all the aging conditions are summarized in Figure 11. The moduli decreased by about 10% at all aging conditions. This decrease in modulus appears to be real; the experimental error for these samples of HDPE-1 was only 2–3% and could be attributable to degradation or plasticization due to “permanent” sorption of some electrolyte components. If degradation was the primary cause for the decrease in modulus, one would expect to observe trends with time and temperature. That no such trends were observed suggests that degradation, if it occurred at all, was minimal.

As shown in Figure 12, similar results were obtained for HDPE-2, though for this electrode the spread in the data was much wider (sigmas for HDPE-2 were ~18% vs. 2–3% for HDPE-1). The larger data scatter observed for HDPE-2 may be attributable to greater heterogeneities in this electrode.

In a further effort to detect degradation of the electrodes, we monitored G' as a function of temperature from ambient to 150°C. The temperature range includes the melting transition of the polyethylene, which is 125°C. The data for HDPE-1 and -2 are shown in Figures 13 and 14, respectively. In the case of HDPE-1, a decrease in modulus was observed at temperatures below 120°C; above this temperature, the modulus was either the same or higher than that of the control. Somewhat differently shaped curves were obtained for HDPE-2. In this case, the moduli were either lower or the same as the control over the entire temperature range. The data above the melting transition are difficult to interpret in terms of degradation that might have occurred during aging and may be an artifact of the test.

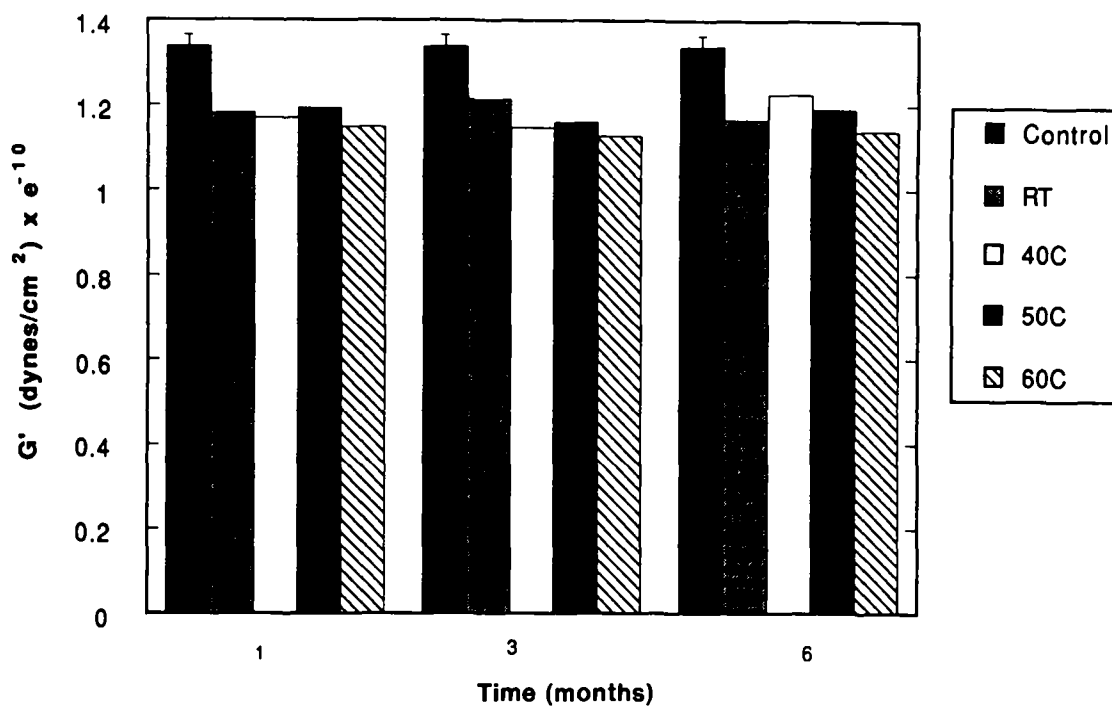


Figure 11. Column plot of the storage modulus (G') as a function of time and temperature for HDPE-1. Data obtained after washing to remove excess electrolyte and after air-drying.

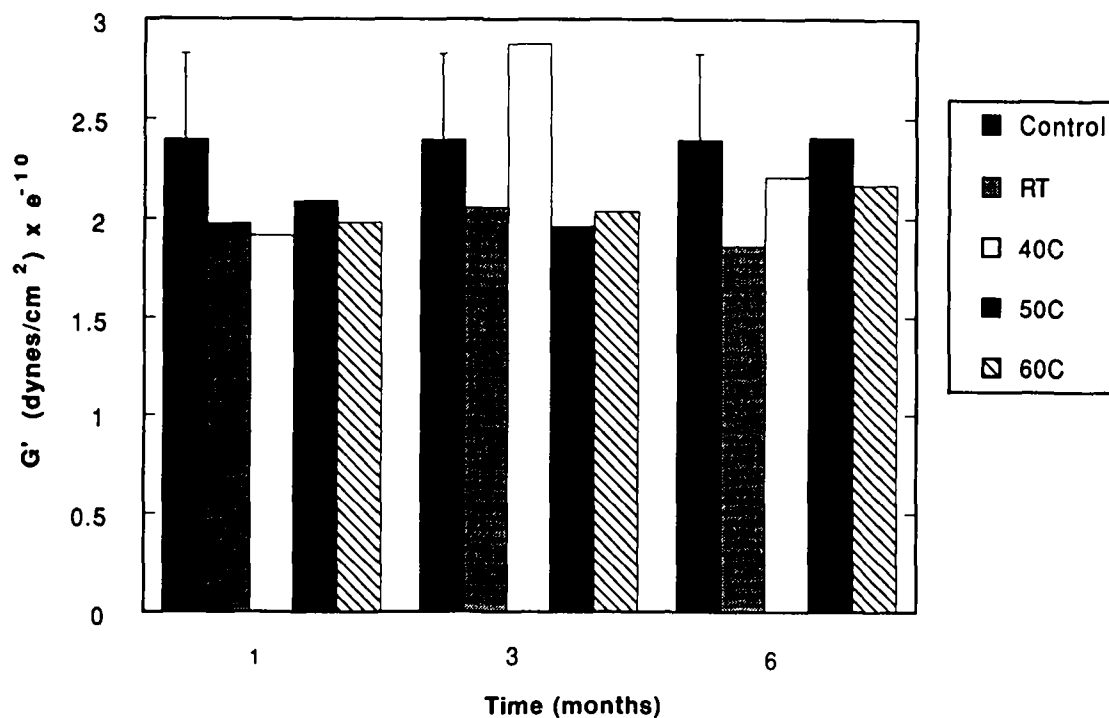


Figure 12. Column plot of the storage modulus (G') as a function of time and temperature for HDPE-2. Data obtained after washing to remove excess electrolyte and after air-drying.

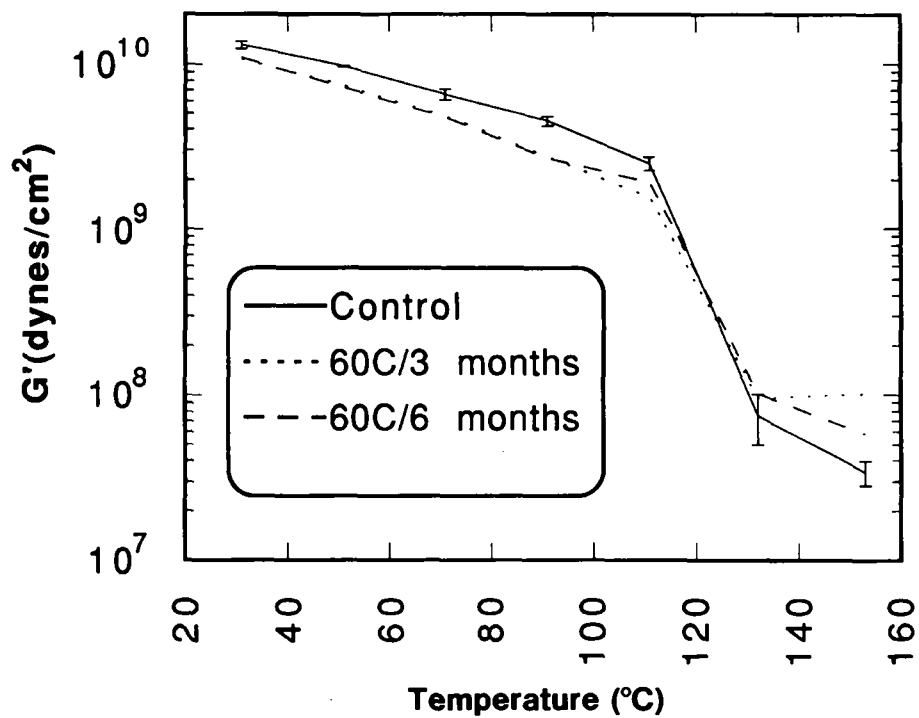


Figure 13. Storage modulus (G') vs. temperature of HDPE-1 after exposure times of 3 and 6 months at 60°C.

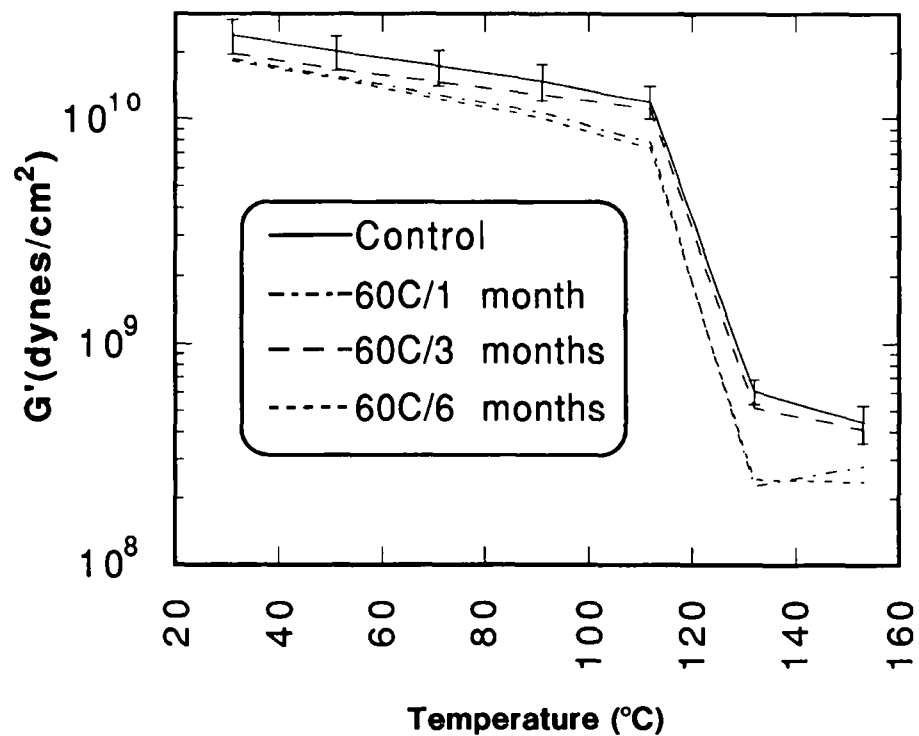


Figure 14. Storage modulus (G') vs. temperature of HDPE-2 after exposure times of 1, 3, and 6 months at 60°C.

Chemical Characterization. In previous accelerated aging studies it was shown that electrodes made from EP copolymers were oxidized by aqueous bromine electrolytes.¹ This conclusion was based primarily on FTIR analyses, which indicated the presence of both carbonyl and hydroxyl moieties after aging. These groups were also detected in electrodes taken from batteries that failed in service. As mentioned in the Introduction, we hypothesized that susceptibility of EP copolymers to oxidative degradation was attributed to the presence of a large number of tertiary hydrogens in the backbone of this polymer. It is well known that tertiary hydrogens are more susceptible to oxidative attack than secondary or primary hydrogens.² It is also well known that high-density polyethylene contains very few tertiary hydrogens, and it was on this basis that this type of polyolefin was recommended as a replacement for the EP copolymers.

The upper curve of Figure 15 is an FTIR spectrum of *unaged* HDPE-1. The peaks at 2912, 2854, and 1465 cm^{-1} are attributable to the CH_2 group of the polyethylene. The small peak at 1710 cm^{-1} is at the frequency for carbonyl groups and is probably attributable to an antioxidant type of additive. One example of an additive having a carbonyl group and widely used as an antioxidant for polyolefins is dilauryl thioldipropionate.⁵ The broad absorption peak in the frequency range of 1100 to 800 cm^{-1} is attributable to the silicate groups of the glass fiber reinforcement. The "noise" in the spectrum at high frequencies is attributable to water vapor. The lower curve is the FTIR spectrum of a sample of HDPE-1 that had been aged in the electrolyte for 6 months at 50°C. Except for a difference in the intensity of the silicate group, the two spectra are virtually identical. One possible explanation for the difference in the silicate band intensity is that the glass fibers are not uniformly distributed in the electrode, and very small samples were used for analysis. Similar results were

obtained for HDPE-2 (Figure 16) except that there was no carbonyl band in either the unaged or aged sample. These results indicate that oxidative degradation of HDPE-1 and -2 did not take place, and that the choice of HDPE as a replacement for the EP copolymers was justified. Furthermore, these results are consistent with the minimal changes observed in the thermal and mechanical properties of the electrodes that were discussed above.

Electrical Conductivity. Data on changes incurred by aging on the electrical conductivity of HDPE-1 and HDPE-2 for 6 months at various temperatures are shown in Figures 17 and 18. To determine if there was any difference between opposite surfaces of the electrodes, data were collected on both surfaces. These surfaces were arbitrarily designated as surface 1 (Figure 17) and surface 2 (Figure 18). Each data point represents an average of four measurements. It is evident that aging increased the conductivity of the electrodes. This of course is very desirable. Conductivity increases ranged from 5% to 48% and were higher for HDPE-1 than for HDPE-2. The higher increase observed for HDPE-1 may be because this electrode has a higher carbon-plastic content and sorbs greater amounts of the electrolyte. The highest increases in conductivity were observed for samples aged at ambient conditions. This observation may be attributed to the fact that these samples had been agitated during aging to ensure good contact with the two-phase electrolyte. Generally, it is believed that the increase in conductivity is due to good wetting of the electrodes by the electrolyte.

It is noteworthy that the conductivity of electrodes made from EP copolymers aged under similar conditions *decreased* by 50%. Hence, when degradation does occur, it has a bad effect on conductivity, which is a very important electrode property.

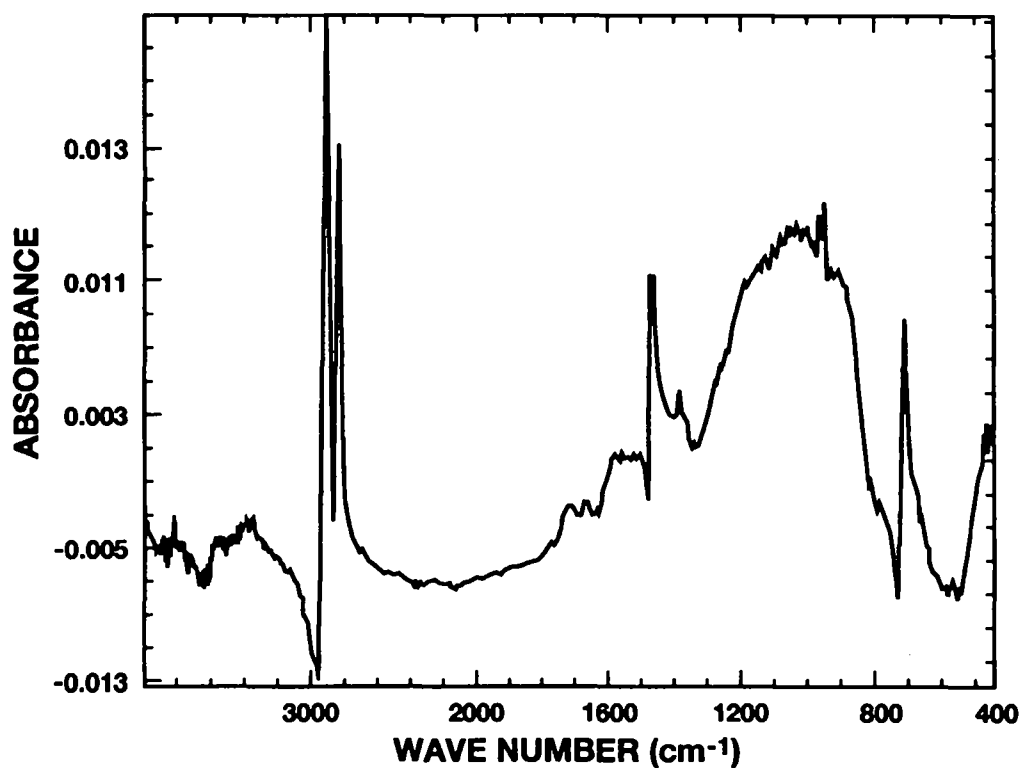
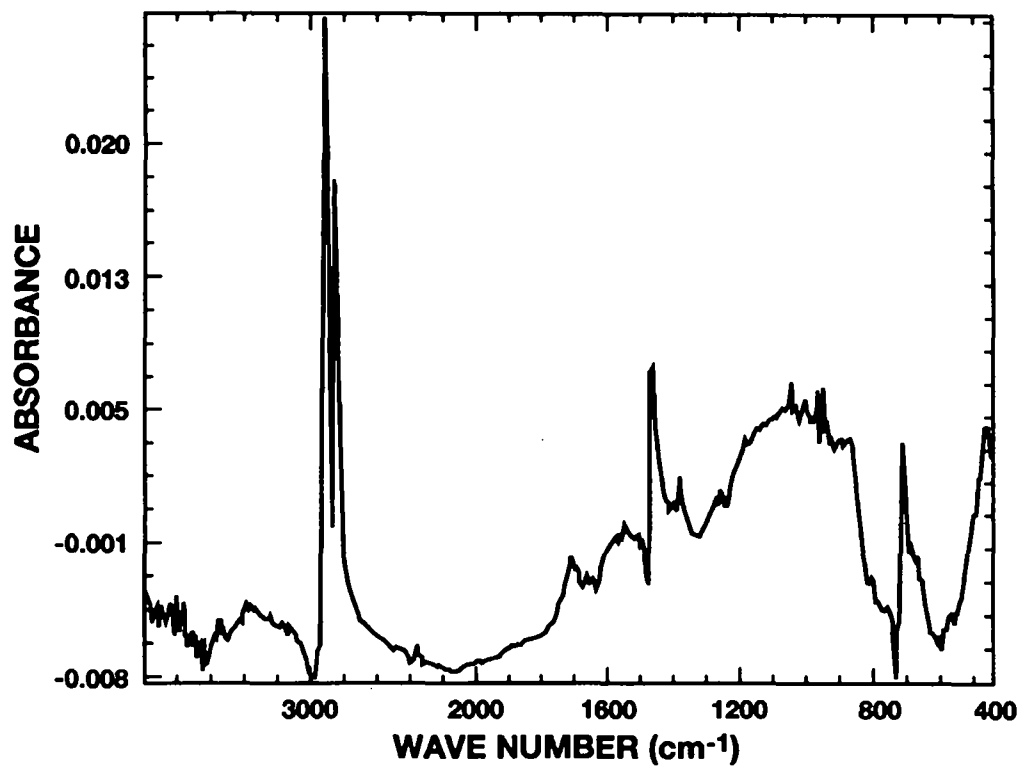


Figure 15. Fourier transform infrared spectra of HDPE-1. Upper spectrum, unaged; lower spectrum, after aging at 60°C for 6 months.

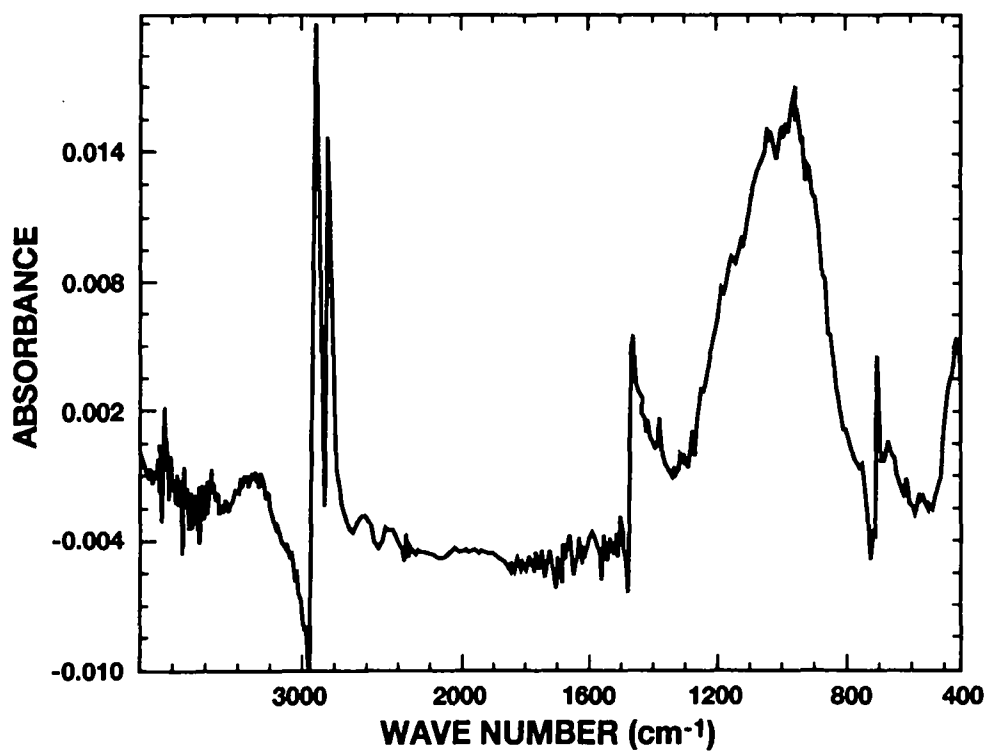
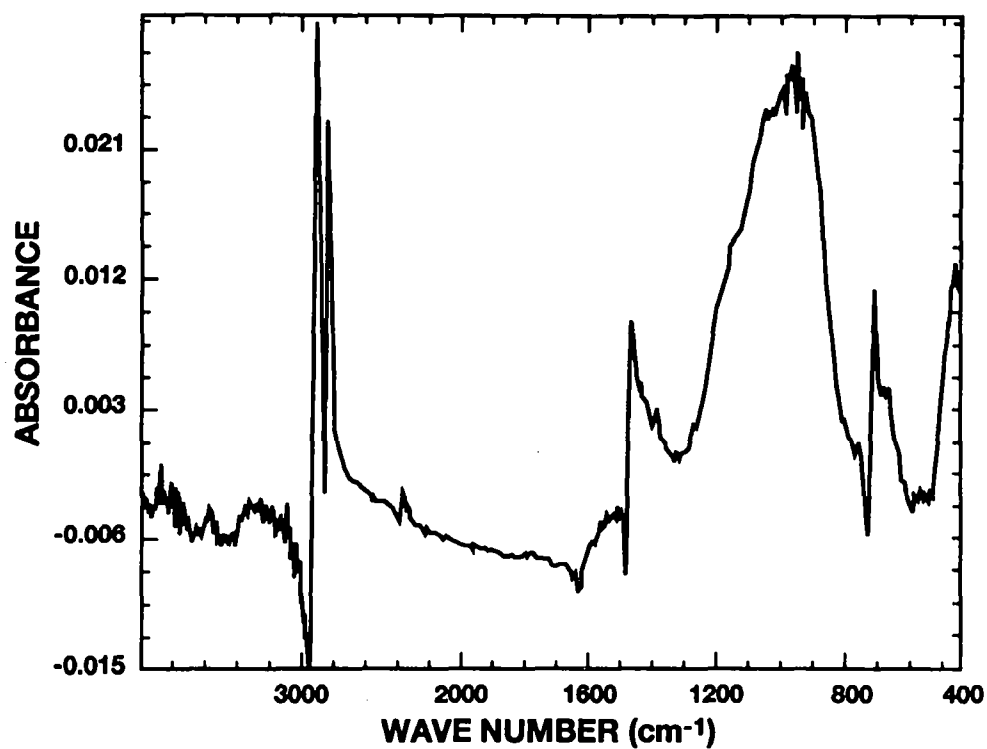


Figure 16. Fourier transform infrared spectra of HDPE-2. Upper spectrum, unaged; lower spectrum, after aging at 60°C for 6 months.

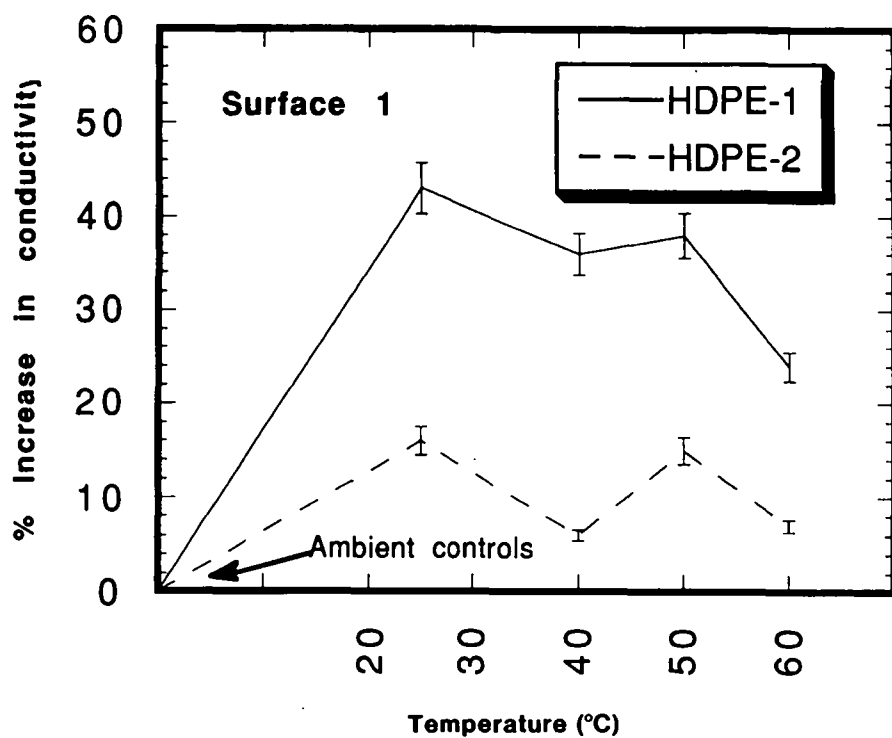


Figure 17. Percent increases of electrical conductivity on surface 1 of HDPE-1 and HDPE-2 after 6 months of aging as a function of temperature.

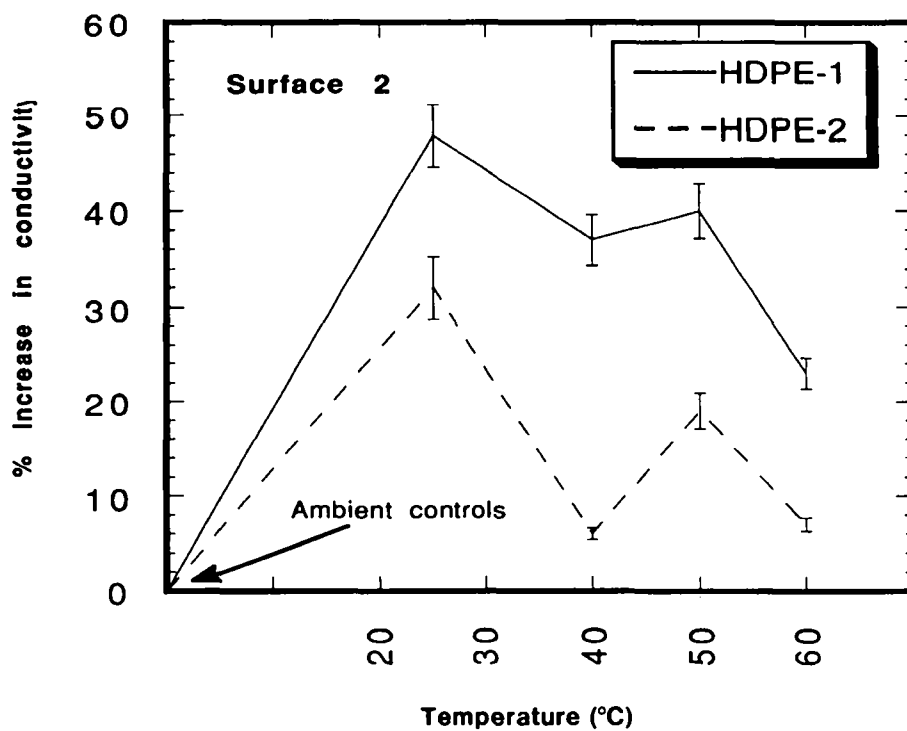


Figure 18. Percent increases of electrical conductivity on surface 2 of HDPE-1 and HDPE-2 after 6 months of aging as a function of temperature.

Conclusions

The following conclusions were drawn from this work:

1. HDPE-2 has a higher glass-filler content than HDPE-1.
2. The glass fibers in both electrodes are rather long (100–500 microns) and not uniformly distributed.
3. Both electrodes strongly absorb some components of the electrolyte that are not salts.
4. Sorption of the non-salt components of the electrolyte decreases with increasing glass-filler content.
5. Increasing the glass-fiber content of the electrode enhances the electrode's dimensional stability in the longer dimensions (i.e., length and width).
6. The mechanical properties of the electrode decrease slightly because of sorption of the electrolyte, not degradation.
7. The crystalline nature of the polyethylene component was not affected by exposure to the electrolyte.
8. Electrodes made from high-density polyethylene were not chemically attacked by the electrolyte.
9. The electrical conductivity of the electrodes increased upon exposure to the electrolyte; in contrast, the conductivity of electrodes made from EP copolymers decreased by 50% under the same conditions.
10. Overall, electrodes made from HDPE appear to have superior long-term stability compared to those fabricated from EP copolymers in the Zn/Br₂ battery environment.

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